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An in-depth study of the use of eosin Y for the solar photocatalytic oxidative coupling of benzylic amines

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KEYWORDS: Photochemistry, photocatalysis, eosin Y, solar, oxidation, imines, amines, design of experiments.

ABSTRACT

The direct utilization of solar light for synthetic photochemistry is a sustainable and efficient technological goal. Herein we report the first in-depth study on the use of the inexpensive and organic photocatalyst, eosin Y, for solar photocatalysis by demonstrating the oxidative coupling

of benzylic amines to form imines, a class of valuable intermediates in chemical synthesis. Using a unique experimental set-up with a custom built variable intensity solar light simulator, replication of a natural sunlight environment has been achieved. The relative significance of different variables on the reaction rate constant has been quantitatively evaluated through comprehensive experimental design. Reaction kinetics and mechanistic information were obtained using both a batch and a spinning disc reactor. A maximum pseudo-first order rate constant of $1.59 \times 10^{-3} \text{ s}^{-1}$ was obtained at a maximum turnover frequency of 192 h^{-1} through optimization of the reaction conditions. Experiments carried out using a spinning disc reactor confirmed that the reaction was not mass transfer limited, but that it was photon transfer limited.

INTRODUCTION

Due to the depletion of fossil fuels and the increasing global energy demand¹, alternative sources of energy will undoubtedly play a greater role in society in future. Solar photocatalysis for the production of fine chemicals is one path towards a more sustainable future that is less reliant on fossil fuels. In terms of chemical synthesis, light can be considered as the ideal ‘green reagent’ as it is renewable, non-toxic and does not generate any waste products. In addition, many photochemical reactions can be carried out under mild conditions using low temperatures as the energy from the photon is targeted at a specific molecule, removing the need to heat the entire reaction mixture, including solvents.² This allows reactions with a high activation energy to be carried out with better control over intermediate selectivity and stability.³

Since UV light constitutes less than 5% of the solar spectrum, it would be ideal to use solar photocatalysts capable of absorbing visible light. Despite the potential economic and environmental benefits, as well as the development of an array of both concentrating and non-

concentrating solar reactors, the application to fine chemical manufacturing still remains limited.⁴ In terms of laboratory-scale synthesis, common visible light photocatalysts are ruthenium or iridium polypyridyl complexes. These are frequently employed for use in single electron photoredox processes and have been reported to be effective at carrying out various redox reactions, cyclisations, arylations and alkylations, among many others.^{5,6} However, they suffer from several drawbacks which are the high cost, scarcity and toxicity of transition metals such as these.⁷ Organic photocatalysts capable of absorbing visible light are also employed in chemical synthesis and are often cheaper and less toxic than their transition metal counterparts.⁸ Eosin Y has $\lambda_{\text{max}} = 539 \text{ nm}$ ⁸ and has been reported to show photocatalytic activity similar to the aforementioned transition metal photocatalysts when in its neutral quinonoid form (Figure 1).⁹ Transformations it has been used for include redox reactions, halogenations, cyclisations and arylations.⁸⁻¹¹

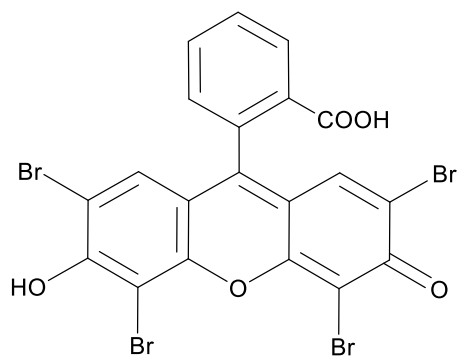


Figure 1 Eosin Y shown in its photochemically active tautomeric form.

Recently there has been much effort put in to developing one-pot oxidative routes towards the synthesis of imines, which are common synthetic intermediates, such as the oxidative coupling of amines.¹² This transformation has previously been reported by non-photocatalytic methods using iron or copper based catalysts, but these syntheses required harsh conditions and/or additives.^{13,14} The synthesis of imines from various substituted benzylamines has previously been

carried out photocatalytically using an iridium polypyridyl complex.¹⁵ In 2010, Condie *et al.* reported the closely related aza-Henry reactions of tertiary amines via selective C-H activation using ruthenium and iridium polypyridyl complexes.¹⁶ König and co-workers showed that the oxidative aza-Henry reactions of tertiary benzylic amines could also be carried out using eosin Y as the photocatalyst.¹⁷ This is a more sustainable alternative to using ruthenium and iridium based photocatalysts as it instead uses a cheap, organic photocatalyst.

For chemical synthesis using visible-light absorbing photocatalysts, there have only been limited studies in to the reaction kinetics and the mechanisms of action.^{16,18,19} Bartling and co-workers have studied the influence of reaction conditions on the kinetics and mechanism of the photocatalytic cross-dehydrogenative coupling of N-aryltetrahydroisoquinolines using a ruthenium polypyridyl photocatalyst in detail.²⁰ A similar example of such a study using eosin Y has been reported in the literature for the aerobic oxidation of thiophenol to phenyl disulphide. Eosin Y loading, reactor configuration and different LED light sources were all shown to affect the yield for the reaction.^{21,22} Consequently, there is a need to systematically evaluate reactions to determine the important parameters affecting the kinetics and gain an insight into the mechanistic pathway. Additionally, photochemical reactions have been shown to have increased efficiency in flow reactors, and in particular microreactors due to increased mass transfer as well as photon transfer, both of which require investigation for photochemical processes.^{23,24}

The aim of this study is therefore to carry out an investigation in to the solar photocatalytic ability of eosin Y for the synthesis of imines, using the oxidative homocoupling of benzylamine to form the imine N-benzylidenebenzylamine as a model reaction. In-depth experimental design will be used to determine the most significant factors affecting the reaction rate constant using a variety of photoreactor set ups.

MATERIALS AND METHODS

Eosin Y (99%, Sigma-Aldrich), benzylamine (98%, Alfa Aesar), 4-methylbenzylamine (98%, Acros Organics), 4-methoxybenzylamine (97%, Fluorochem) and 4-(trifluoromethyl)benzylamine (98%, Fluorochem) were purchased from commercial sources. All solvents were purchased from VWR and used as supplied. A 50 W LED floodlight lamp (Techbox) was used for the initial kinetic studies. The 1200W solar light simulator (SunTech Group AB, Sweden) is a custom built light source, specifically designed to emulate the spectral emission of radiation from the sun. Mapping of the light intensity under the solar light simulator was carried out using an Isotech ILM-1335 light intensity meter at different points along a two dimensional grid for three different heights below the lamp. Light intensity was measured in units of lux but was converted to Wm^{-2} as the luminous efficacy of the lamp was known to be 90 lumens per Watt. All reactions were monitored by ^1H NMR spectroscopy in acetonitrile using a solvent suppression technique. Synthetic procedures and characterisation data are given in the supplementary information.

50 W LED Lamp

For the initial experiments using a 50 W LED lamp, the reactor set up was based on those observed in the literature for photochemical batch reactions.²⁵ A 190 mm diameter glass dish was covered with a sheet of 4 mm thick glass to prevent loss of solvent by evaporation. The lamp was positioned so that the reaction mixture was illuminated from directly above (see Figure 2). The light intensity at the surface of the reaction using this lamp was 43 Wm^{-2} .

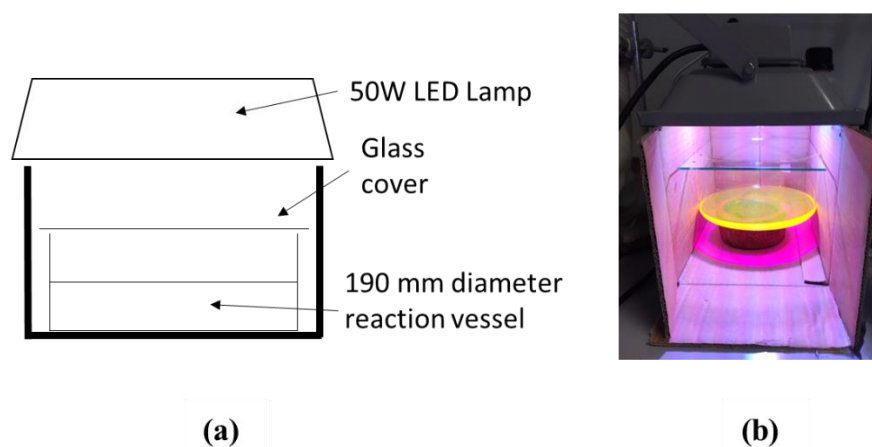


Figure 2 Reaction set up using 50 W LED lamp showing (a) schematic diagram (b) photograph of batch reactor.

Solar light simulator batch experiments

The experimental set up for the solar light simulator is shown in Figure 3. Two reaction vessels were filled and covered with 4 mm thick sheets of glass. A water bath was used to control temperature and the lamp was placed directly above to mimic the geometry of sunlight. The height was adjustable in order to obtain different light intensities (1000 , 778 and 500 Wm^{-2} at 40 , 55 and 70 cm respectively). A UV light filter (SunTech Group AB) was placed below the lamp. Benzylamine was added to a solution of eosin Y in acetonitrile and the reaction was stirred at the required temperature. Aliquots of 0.3 mL of the reaction mixture were taken after 5 , 10 , 15 , 30 ,

45 and 60 minutes and analyzed directly using solvent suppression ^1H NMR.

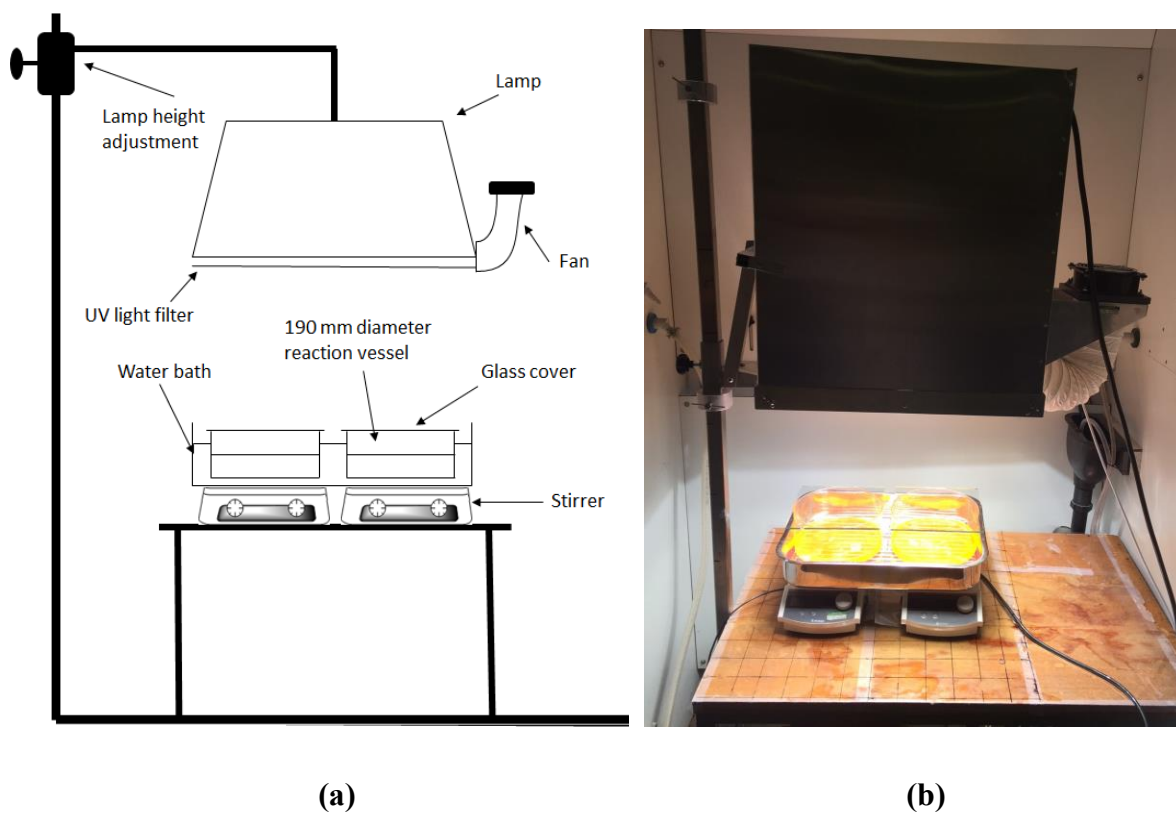


Figure 3 Reactor set up for solar light simulator using batch reactors showing (a) schematic diagram (b) photograph of batch reactor set up.

Solar light simulator spinning disc experiments

The spinning disc reactor (SDR) was set up in a similar way to the batch experiments with the adjustable lamp placed directly above the reactor (Figure 4). The unit housing the disc was covered with a 4 mm thick sheet of glass and was set up according to previously reported procedures.²⁶ The reservoir below the disc was covered to prevent unwanted irradiation from the lamp, allowing a comparison to be made with batch experiments with the same surface area as the disc.

The rotational speed of the disc and the flow rate could be varied. The film thickness of the liquid on the disc was calculated using the Nusselt model (equation 1), which relates the film thickness, h , to the radius, r , volumetric flow rate, Q , kinematic viscosity²⁷, ν , and rotational speed, ω .²⁶

$$h = \left(\frac{3Q\nu}{2\pi r^2 \omega^2} \right)^{\frac{1}{3}} \quad (1)$$

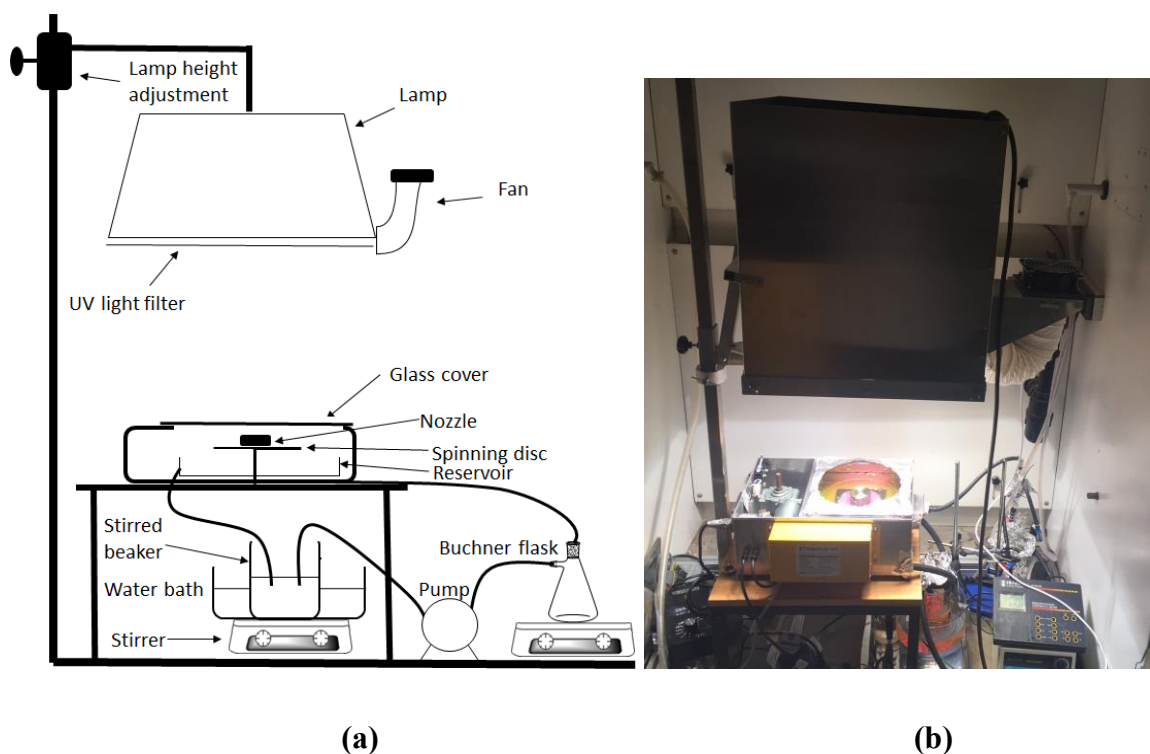


Figure 4 Reactor set up for solar light simulator using spinning disc reactor showing (a) schematic diagram (b) photograph of reactor set up.

Design of Experiments

In order to analyze the factors affecting the rate of reaction, a Design of Experiments (DoE) approach was taken. In this study, a six factor, two level half factorial design with 4 central experiments was chosen, requiring a total of 36 experiments. This is classed as resolution VI,

meaning that the effects of all the variables on their own, as well as multiple interaction variables were able to be analyzed. The experiments were carried out in a random order to minimize systematic errors such as slight degradation of the bulb over time.

Photonic Efficiency

The average photonic efficiencies of the reactions were also calculated using the first order rate constant at the initial concentration. The number of moles of photons incident on the reactor per second was calculated using equation 2²⁸:

$$\text{incident photons (mol s}^{-1}\text{)} = \frac{\text{Irradiance} \times A \times \lambda}{N_A \times hc} \quad (2)$$

where irradiance is in Wm^{-2} , A is area (m^2), λ is wavelength (m), N_A is Avogadro's number (6.02×10^{23}), h is Planck's constant (6.63×10^{-34} Js) and c is the speed of light in a vacuum ($3.00 \times 10^8 \text{ ms}^{-1}$). The photonic efficiency, ζ , was then calculated according to equation 3:

$$\zeta = \frac{\text{rate of reaction}}{\text{incident photons}} = \frac{k \times [B]}{\text{incident photons}} \quad (3)$$

where k is the pseudo-first order rate constant and [B] is the initial concentration of benzylamine.

RESULTS AND DISCUSSION

Initial Experiments to establish reaction conditions (50W LED Lamp)

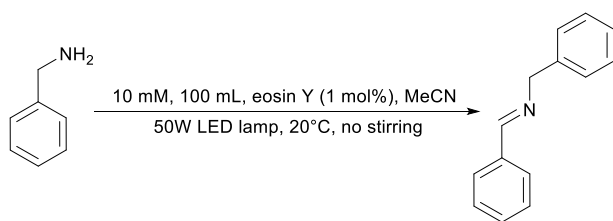
In order to establish suitable reaction conditions for the photocatalytic oxidative homocoupling of benzylamine, a series of experiments were carried out to determine the effect of reactor geometry, reaction volume, temperature and catalyst and reactant concentrations on the reaction conversion after a number of hours (See Supplementary Information). Higher conversions were achieved at higher surface area to volume ratios and temperatures, with the relationship between

reactant and catalyst concentrations appearing to be more complex. The surface area dependence suggests that the light is unable to penetrate completely through the solution.

Reactions were also carried out in the absence of light, oxygen and eosin Y. These did not show any conversion to the imine product, indicating that these three factors are all required for the reaction to take place, which is in accordance with mechanisms which have been suggested in the literature for amine oxidation by eosin Y.^{8,17}

Kinetic NMR Study

To investigate the reaction order in benzylamine, an experiment was carried out over an 8 hour period and monitored by ¹H NMR (Scheme 1). The results in Figure 5 show that saturation kinetics were observed for the first part of the reaction, with the reaction appearing to be zero order in benzylamine. Once the concentration reached approximately 6 mM then first order kinetics were observed, with a pseudo-first order rate constant equal to $5 \times 10^{-5} \text{ s}^{-1}$. The saturation kinetics observed above 6 mM suggests that the reaction was limited by the power of the lamp as not enough light was reaching the reaction. It was hoped that by increasing the light intensity at the reaction surface, the reaction would cease to become limited by the amount of light reaching it. Catalyst decomposition may also be occurring due to the long reaction time and it was also hoped that a more powerful light source would allow shorter reaction times to minimize this effect. Additionally, it was observed that after the reaction had reached 95% conversion of starting material, other peaks were present in the NMR spectra. There were some additional signals in the aromatic region but also, most notably, a peak at around 10 ppm indicated the presence of some benzaldehyde which was thought to have been formed by an over-oxidation of the product due to the presence of water.



Scheme 1 Reaction conditions used for the kinetic investigation of photooxidation of benzylamine to N-benzylidenebenzylamine.

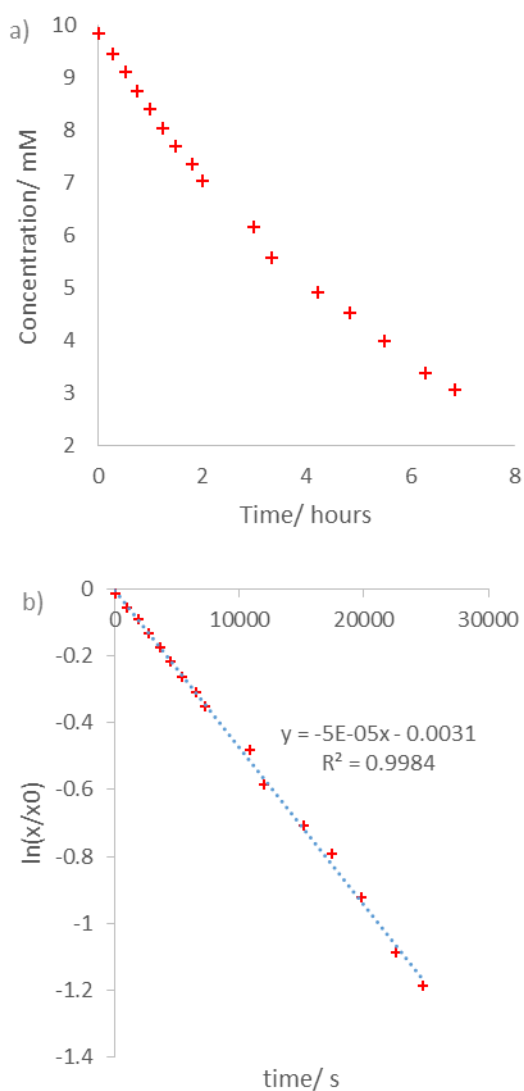


Figure 5 Conversion of benzylamine to N-benzylidenebenzylamine monitored by ^1H NMR a) concentration vs. time b) first order kinetic logarithmic plot.

Design of Experiments Study (Solar Light Simulator)

Using the 1200W solar light simulator, the reaction time was reduced to approximately 1 hour (depending on other reaction parameters). A half factorial experimental design was created using Minitab Statistical software consisting of six variables, each with two levels, plus four central points, giving a total of 36 experiments. The results of the DoE study are shown in Table 1, which also indicates the high, intermediate and low levels of each of the factor. A linear relationship was observed for all of the first order logarithmic kinetic plots during the DoE study, allowing a pseudo-first order rate constant to be calculated. Photonic efficiencies were also calculated using the light intensity measured during each experiment. Representative plots of conversion against time for two different light intensities are shown in Figure 6.

Table 1 Results of Design of Experiments study for photocatalytic reaction of benzylamine to form N-benzylidenebenzylamine using eosin Y as photocatalyst and solar light simulator. Conversions stated are after 1 hour of reaction.

| Entry | Light intensity/ Wm ⁻² | T/ °C | Amine conc./ mM | Eosin mol % | Vol/ mL | Stir speed/ rpm | Conversion | mmol reacted | TOF / h ⁻¹ | Rate constant/ x 10 ⁻⁴ s ⁻¹ | Photonic Efficiency / x 10 ⁻³ |
|-------|--------------------------------------|----------|--------------------|-------------|------------|--------------------|------------|--------------|-----------------------|--|--|
| 1 | 555 | 0 | 5 | 0.5 | 100 | 0 | 71.9% | 0.36 | 144 | 3.5 | 1.67 |
| 2 | 1000 | 0 | 5 | 0.5 | 100 | 500 | 88.5% | 0.44 | 177 | 6.0 | 5.04 |
| 3 | 555 | 40 | 5 | 0.5 | 100 | 500 | 79.5% | 0.40 | 159 | 4.4 | 2.77 |
| 4 | 1000 | 40 | 5 | 0.5 | 100 | 0 | 95.7% | 0.48 | 192 | 8.7 | 1.91 |
| 5 | 555 | 0 | 15 | 0.5 | 100 | 500 | 63.2% | 0.95 | 126 | 2.8 | 1.42 |
| 6 | 1000 | 0 | 15 | 0.5 | 100 | 0 | 87.2% | 1.31 | 174 | 5.6 | 3.42 |
| 7 | 555 | 40 | 15 | 0.5 | 100 | 0 | 69.4% | 1.04 | 139 | 3.3 | 3.38 |
| 8 | 1000 | 40 | 15 | 0.5 | 100 | 500 | 91.2% | 1.37 | 182 | 6.8 | 3.01 |
| 9 | 555 | 0 | 5 | 1.5 | 100 | 500 | 89.6% | 0.45 | 60 | 6.3 | 3.45 |
| 10 | 1000 | 0 | 5 | 1.5 | 100 | 0 | 98.4% | 0.49 | 66 | 11.4 | 0.90 |
| 11 | 555 | 40 | 5 | 1.5 | 100 | 0 | 94.7% | 0.47 | 63 | 8.4 | 8.92 |
| 12 | 1000 | 40 | 5 | 1.5 | 100 | 500 | 99.7% | 0.50 | 66 | 15.9 | 3.47 |
| 13 | 555 | 0 | 15 | 1.5 | 100 | 0 | 60.9% | 0.91 | 41 | 2.6 | 2.25 |
| 14 | 1000 | 0 | 15 | 1.5 | 100 | 500 | 87.7% | 1.32 | 58 | 5.9 | 3.32 |
| 15 | 555 | 40 | 15 | 1.5 | 100 | 500 | 87.0% | 1.31 | 58 | 5.4 | 1.31 |
| 16 | 1000 | 40 | 15 | 1.5 | 100 | 0 | 99.3% | 1.49 | 66 | 13.4 | 1.01 |
| 17 | 555 | 0 | 5 | 0.5 | 200 | 500 | 52.6% | 0.53 | 105 | 2.1 | 2.92 |
| 18 | 1000 | 0 | 5 | 0.5 | 200 | 0 | 70.1% | 0.70 | 140 | 3.3 | 1.72 |
| 19 | 555 | 40 | 5 | 0.5 | 200 | 0 | 61.9% | 0.62 | 124 | 2.7 | 2.65 |
| 20 | 1000 | 40 | 5 | 0.5 | 200 | 500 | 82.6% | 0.83 | 165 | 4.8 | 0.97 |
| 21 | 555 | 0 | 15 | 0.5 | 200 | 0 | 54.3% | 1.63 | 109 | 2.2 | 4.75 |
| 22 | 1000 | 0 | 15 | 0.5 | 200 | 500 | 80.0% | 2.40 | 160 | 4.5 | 5.99 |
| 23 | 555 | 40 | 15 | 0.5 | 200 | 500 | 65.4% | 1.96 | 131 | 3.0 | 7.14 |
| 24 | 1000 | 40 | 15 | 0.5 | 200 | 0 | 83.0% | 2.49 | 166 | 5.0 | 3.47 |
| 25 | 555 | 0 | 5 | 1.5 | 200 | 0 | 80.2% | 0.80 | 53 | 4.6 | 1.00 |
| 26 | 1000 | 0 | 5 | 1.5 | 200 | 500 | 94.4% | 0.94 | 63 | 8.0 | 4.77 |
| 27 | 555 | 40 | 5 | 1.5 | 200 | 500 | 86.7% | 0.87 | 58 | 5.6 | 1.48 |
| 28 | 1000 | 40 | 5 | 1.5 | 200 | 0 | 97.4% | 0.97 | 65 | 10.4 | 5.77 |
| 29 | 555 | 0 | 15 | 1.5 | 200 | 500 | 52.9% | 1.59 | 35 | 2.1 | 3.79 |
| 30 | 1000 | 0 | 15 | 1.5 | 200 | 0 | 78.6% | 2.36 | 55 | 4.1 | 5.98 |
| 31 | 555 | 40 | 15 | 1.5 | 200 | 0 | 81.7% | 2.45 | 55 | 4.8 | 2.66 |
| 32 | 1000 | 40 | 15 | 1.5 | 200 | 500 | 98.6% | 2.96 | 66 | 11.5 | 1.45 |
| 33 | 778 | 20 | 10 | 1 | 150 | 250 | 84.4% | 1.27 | 84 | 5.1 | 3.15 |
| 34 | 778 | 20 | 10 | 1 | 150 | 250 | 84.4% | 1.27 | 84 | 5.2 | 1.91 |
| 35 | 778 | 20 | 10 | 1 | 150 | 250 | 82.1% | 1.23 | 82 | 4.7 | 4.86 |
| 36 | 778 | 20 | 10 | 1 | 150 | 250 | 83.0% | 1.25 | 83 | 4.9 | 1.97 |

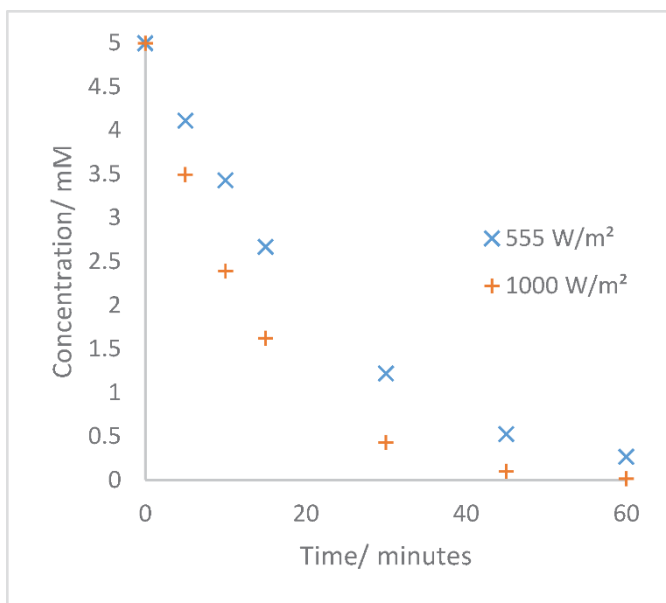


Figure 6 Conversion of benzylamine to N-benzylidenebenzylamine using solar light simulator under two different light intensities (entries 11 and 12 in Table 1). Stir speed also differs between the two but stirring was not shown to have a significant impact on the rate constant (see below).

Significant Factors Affecting Rate of Reaction

For the analysis of the significance of different variables, a suitable output had to be chosen. There were several responses which could be used in order to analyze the effects of the variables and the interactions between them, and these are included in Table 1. The total number of moles of benzylamine reacting and turnover frequency were considered unsuitable as they were heavily weighted by single factors (amount of amine and catalyst present initially). Conversion after a given time was more suitable but relied on a single data point. For these reasons, the pseudo-first order rate constant was chosen. The normal plot and Pareto chart for the DoE results using rate constant as the response variable are shown in Figures 7 and 8. The Pareto chart plots the factors in order of significance by their standardized effect on the rate constant, with the dotted line signifying 5% significance.

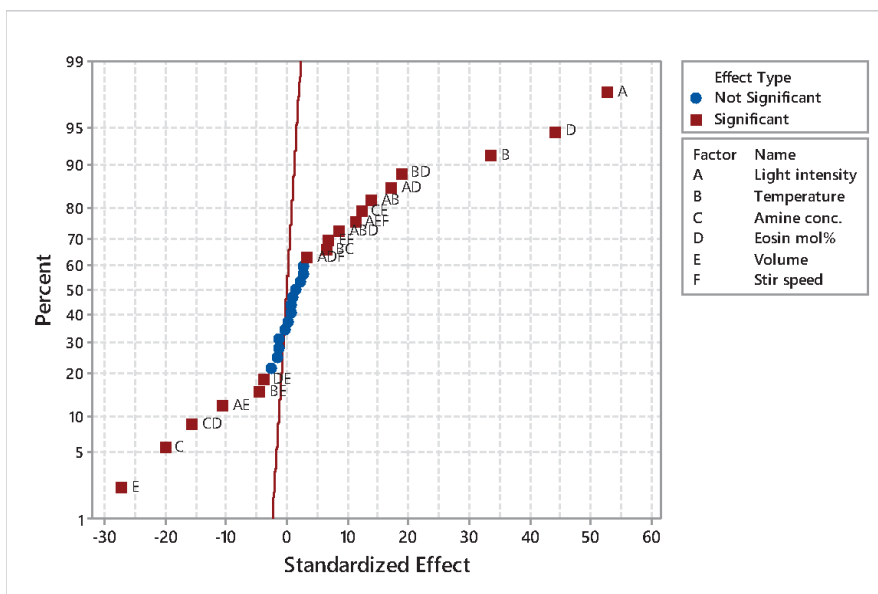


Figure 7 Normal plot showing the magnitude and sign of the standardized effect of different factors on the first order rate constant.

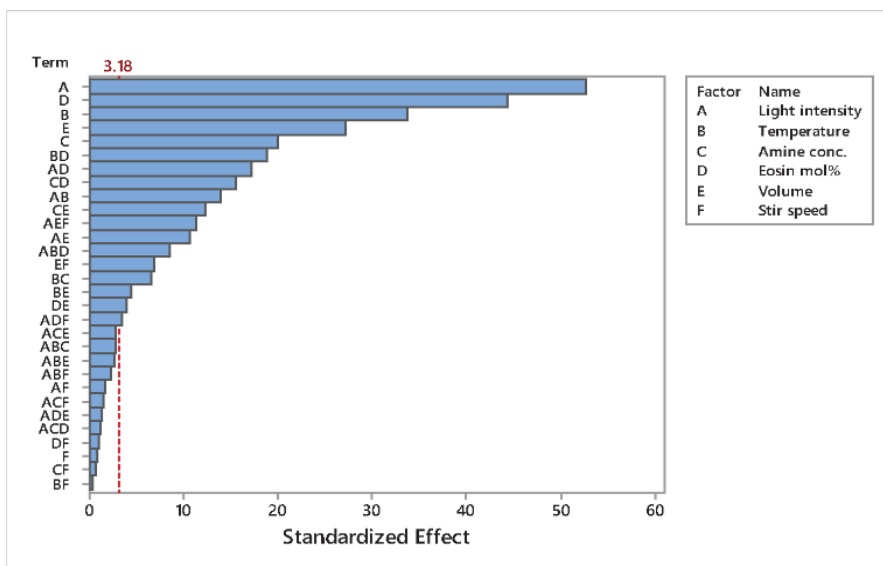


Figure 8 Pareto plot showing the order and magnitude of the standardized effect of different factors on the first order rate constant.

Overall, the results indicate that the light intensity, eosin mol %, temperature and the volume are the most important single factors (in order), with the remaining factors all fairly closely gathered after that. This confirmed the earlier findings that light intensity was the limiting factor in the reaction. Increasing the catalyst loading also significantly increased the rate, which was different to previous findings using the less powerful 50 W LED lamp. This suggests that due to the higher photon flux available from the solar light simulator, other factors which were previously insignificant such as catalyst loading now play a greater role in determining reaction rate. Increasing temperature also increased the rate, which was in agreement with previous findings. This was expected to be due to acceleration of the non-photochemical steps which follow the initial oxidation by eosin Y (Scheme 2).

The fact that a lower volume gave a greater rate of reaction without changing concentration suggests that only the top layer of reaction was able to utilize the incoming light. This would also support the observation that light intensity was rate limiting, as a higher flux of photons would mean that the light may not be able to penetrate deeper in to solution. These results suggest that having a larger surface area to volume ratio, such as with a wider reactor or a reactor which creates a thin film such as the spinning disc reactor should lead to an increase in rate.

A lower amine concentration gave a greater first order rate constant. One would expect the rate constant to be independent of concentration, although the rate itself would be affected. This result was possibly due to the solution being more opaque as the amine concentration was increased and therefore not allowing the light to penetrate as far through the solution to be absorbed by the photocatalyst. Since photocatalytic reactions are pseudo-first order due to limitations by photon absorption²⁹, it follows that penetration of light through solution is an important factor in affecting the rate constant.

Stirring was not observed to have a significant effect on the rate, suggesting that the reaction was not limited by mass transfer. Even though light is suspected to only penetrate through a certain depth of solution, diffusion to the surface was likely fast enough that stirring did not have any significant effect on the reaction.

Finally, the results indicate that combinations of variables also have a compounded effect on the reaction rate. Increasing multiple factors at the same time, such as temperature, light intensity or catalyst loading, increase the rate of reaction by a greater amount than can be accounted for by simply increasing each of these on their own.

Overall, the rate constants obtained spanned an order of magnitude. The greatest rate constant of $1.59 \times 10^{-3} \text{ s}^{-1}$ was obtained with the values of each variable that would be predicted based on the results, i.e. highest light intensity, temperature and eosin Y mol % but lowest amine conc. and volume. Note that it was also stirred at 500 rpm but that stirring was not seen to be a significant factor.

To the best of the authors' knowledge, there have not been any studies on the photonic efficiency of the photocatalytic oxidative homocoupling of benzylamine so far in the literature and so there are no results to compare this reactor set up to. The results suggest that this reactor configuration allows effective absorption of light by eosin Y and that light intensity is the limiting factor. This is reflected by the photonic efficiencies as they are relatively independent of light intensity, lying between 0.1 – 0.9%.

Effect of Surface Area to Volume Ratio

All of the previous reactions had been carried out in the 190 mm diameter reaction vessel for consistency between results. However, since volume and light intensity had been shown to be

significant factors in determining the rate, it follows that increasing surface area to volume ratio (which is affected by volume for a single reactor geometry) should increase the rate of reaction. Therefore, an identical reaction was carried out in three different reactors, all made from glass but with different surface areas. The solution depth was also measured and the results are shown in Table 2. A clear trend is observed in that increasing surface area (or decreasing depth), causes an increase in rate constant. This is due to a larger area being irradiated and therefore a larger amount of light being able to be absorbed by eosin Y to catalyze the reaction. Figure 9 shows the approximately linear relationship between surface area and reaction rate constant. One would expect this graph to level off at some point once the depth of solution is equal to the depth that the light is able to penetrate through, as increasing surface area after this point would not allow any more light to be absorbed.

Table 2 Results obtained using different reactor geometries to investigate the effect of surface area on the rate of reaction. Reaction conditions used were 400 mL of a 5mM benzylamine solution in acetonitrile with eosin Y (1.5%), artificial sunlight lamp (1000 Wm^{-2}) at 40°C for 1 hour with 500 rpm stirring.

| Surface area/ cm^2 | Depth/ cm | Conversion | mmol reacted | TOF/ h^{-1} | Rate constant/ s^{-1} |
|--------------------------------|--------------|------------|--------------|-------------------------|-----------------------------------|
| 284 | 2.0 | 89.0% | 1.78 | 59 | 6.17×10^{-4} |
| 415 | 1.5 | 93.1% | 1.86 | 62 | 7.38×10^{-4} |
| 816 | 1.0 | 98.9% | 1.98 | 66 | 1.24×10^{-3} |

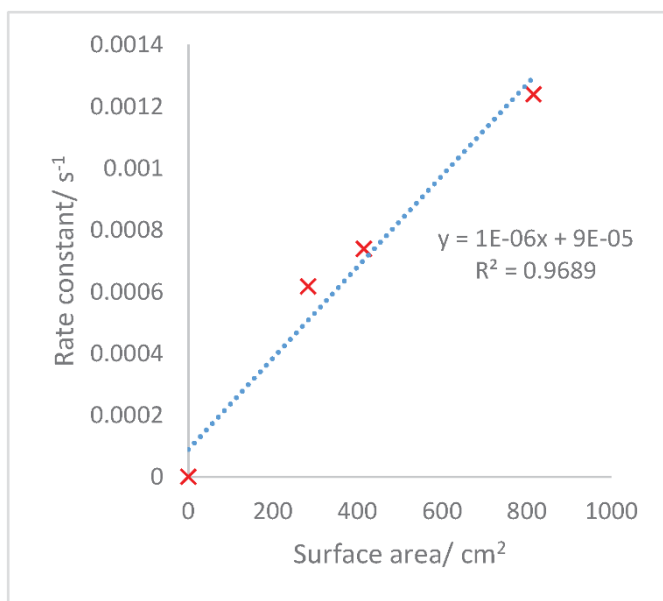


Figure 9 Rate constant dependence on surface area of reactor.

Spinning Disc Reactor

Su *et al.* have shown that photocatalytic reaction rates involving eosin Y can be improved by varying reactor geometry.²² As surface area and depth had been shown to play an important role in determining reaction rate thus far, it was decided to carry out the reaction using a spinning disc reactor as this had previously been shown to be advantageous for photocatalytic systems due to the creation of thin films.²⁶ A larger volume of solution (800 mL) was required for the spinning disc reactor due to much of the solution being pumped round the apparatus and the reservoir at any given time. An equivalent batch process with the same volume and surface area was carried out for comparison. The film thickness was calculated using the Nusselt model and the results are shown in Table 3.

The batch reaction gave a first order rate constant of $4.19 \times 10^{-4} \text{ s}^{-1}$. This was lower than the corresponding 400 mL reaction, as expected due to a lower surface area to volume ratio, but also

corresponded to the largest amount of imine that had been produced in a single experiment in one hour, 3.28 mmol.

The rate of reaction using the SDR was much lower, $2.08 \times 10^{-4} \text{ s}^{-1}$. These results are contradictory to previous work utilizing the SDR, but this was thought to be because, despite the higher surface area to volume ratio, the thickness of the film was less than the depth of solution that the light was able to penetrate through. In previous work the photocatalyst had been immobilized on the disk and was therefore always irradiated.³⁰ For the homogeneous reaction involving eosin Y, at any given time, most of the reaction mixture was in the reservoir or being pumped through the reactor, and therefore not being irradiated. In an attempt to improve the rate, conditions were used which should give the thickest film possible using this reactor. The slowest spin speed and fastest flow rate gave a greater rate constant of $2.72 \times 10^{-4} \text{ s}^{-1}$, showing that a thicker film gave a greater rate constant. One might expect the optimum rate to be achieved when the film thickness equals the depth that light is able to penetrate in solution. However, this was the thickest film possible with this reactor. Additionally, turbulent flow regimes on the disc may actually decrease the rate of reaction when compared to the batch for photon transfer limited reactions, despite creation of a thin film.³⁰ Future work within the group will examine immobilization of the catalyst to improve light absorption, catalyst separation and potential recycling.

Table 3 Effect of using the spinning disc reactor with varying spin speed and flow rate on the rate of reaction. Reaction conditions used were 800 mL of a 5mM benzylamine solution in acetonitrile with eosin Y (1.5%), artificial sunlight lamp (1000 Wm^{-2}) at 40°C for 1 hour (with 500 rpm stirring in batch).

| Reactor | Spin speed/ rpm | Flow rate/ mL s ⁻¹ | Film depth/ mm | mmol reacted | TOF/ h ⁻¹ | Rate constant/ x 10 ⁻⁴ s ⁻¹ |
|---------|--------------------|----------------------------------|-------------------|--------------|-------------------------|--|
| batch | - | - | - | 3.28 | 55 | 4.19 |
| SDR | 300 | 15 | 0.252 | 2.11 | 35 | 2.08 |
| SDR | 100 | 25 | 0.431 | 2.49 | 41.5 | 2.72 |

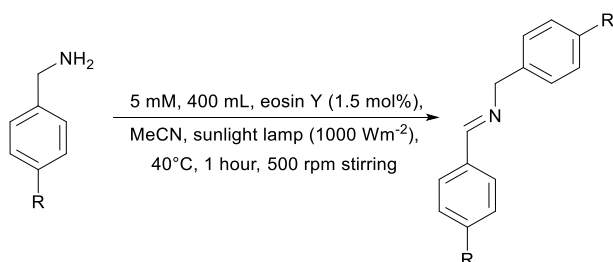
Effect of Ring Substituents

The rate constants for different *para*-substituted benzylamines were obtained using the same analytical NMR method and batch set up with 190 mm diameter reactors and the 1200 W lamp as previously (Figure 3), with the results being shown in Table 4. The trifluoromethyl and chlorine groups lowered the rate constant due to withdrawing electron density from the benzylic carbon, thus making oxidation by eosin Y more difficult. The opposite was true for the electron donating groups, with the methoxy and methyl groups both increasing the rate due to donating electron density, making oxidation by eosin Y easier. Using these initial results and σ values obtained from Hansch *et al.*,³¹ an exploratory Hammett plot of the results was constructed and is shown in Figure 10. The ρ value was found to be -0.9, indicating a build-up of positive charge at the transition state during the rate determining step of the reaction. These results were supportive of mechanisms of oxidation by eosin Y in the literature with the initial oxidation being rate limiting.⁸

The proposed mechanism in Scheme 2 builds upon suggested mechanisms in the literature for amine oxidation^{17,32}. The results are also consistent with the findings of Murray *et al.* for the same reaction of benzylamines but catalyzed by a synthetic flavin.³² They found $\rho = -2$, suggesting that the reaction mechanism with eosin Y as photocatalyst is similar to that of the flavin in that they both involve oxidation of the benzylamine by the catalyst initially. However, it appears that eosin Y is less sensitive to the electronics of the ring. This could be due to the

greater dependence of eosin on light intensity compared to the flavin, and photon transfer being limiting in this case.

Table 4 Rate constants and conversions after 1 hour obtained for the photocatalytic oxidative homocoupling of substituted benzylamines.



| R | Conversion | Rate constant/ $\times 10^{-4} \text{ s}^{-1}$ |
|-----------------|------------|--|
| H | 89.0% | 6.17 |
| Me | 98.7% | 8.13 |
| OMe | 91.8% | 6.92 |
| Cl | 80.0% | 4.35 |
| CF ₃ | 89.2% | 3.94 |

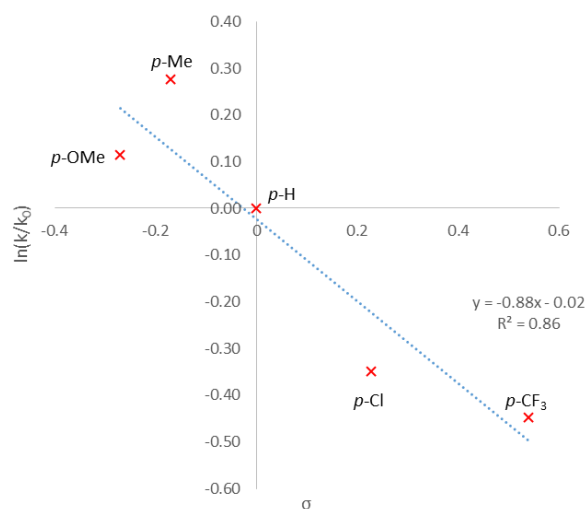
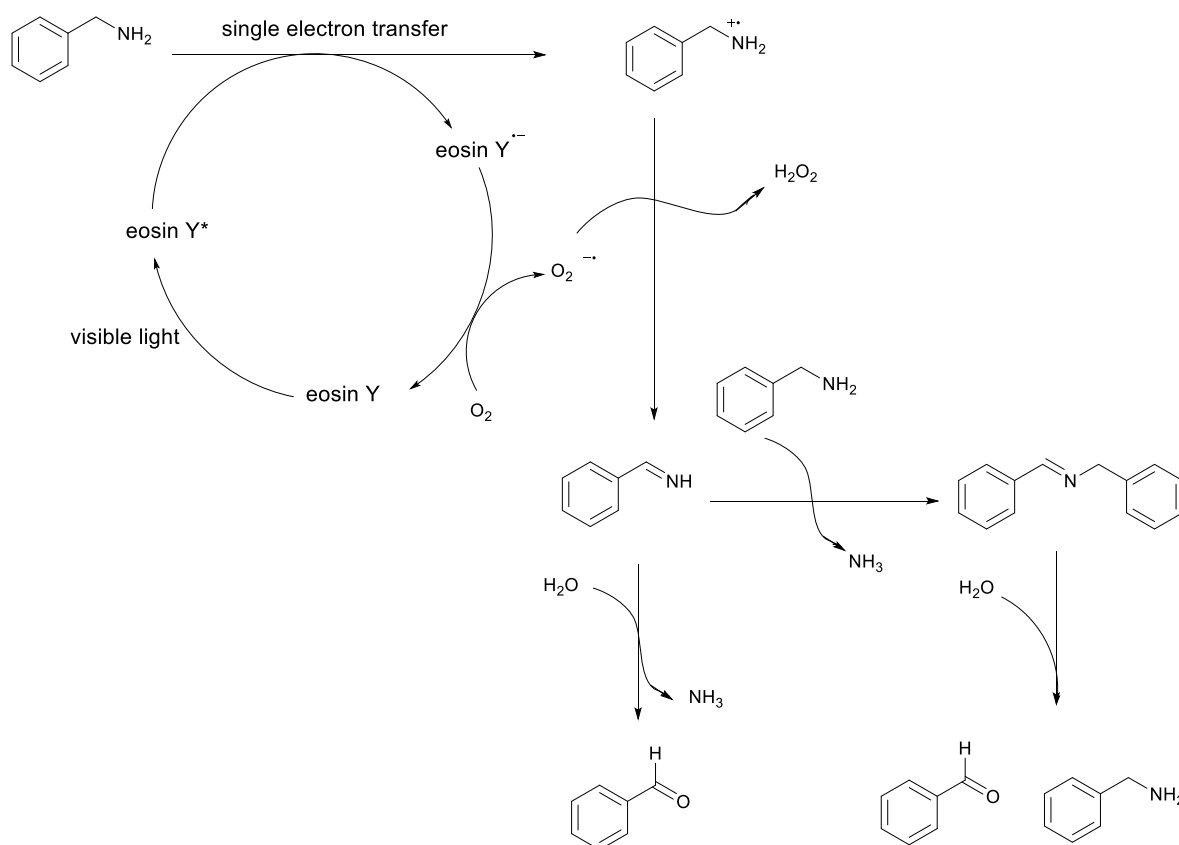


Figure 10 Hammett plot showing the effect of different ring substituents on the rate of reaction.



Scheme 2 Proposed mechanism for the formation of N-benzylidenebenzylamine from benzylamine using eosin Y as photocatalyst, as well as the formation of benzaldehyde from the product and the intermediate.

Conclusions

This work is the first in-depth kinetic study in to the photocatalytic oxidative homocoupling of benzylamine using eosin Y as a photocatalyst and simulated sunlight. The reaction showed pseudo-first order kinetics and through a half factorial design of experiments study, the most significant factors affecting the first order rate constant were determined.

The spinning disc reactor was not observed to increase the rate of reaction when compared to a corresponding batch experiment. This supports the theory that the reaction is not mass transfer

limited and future research will focus on immobilization of the photocatalyst on the disc. The reaction showed a strong surface area dependence, supporting the findings that light intensity throughout the reacting solution is the limiting factor.

Overall, eosin Y shows promise as a sustainable, metal-free photocatalyst for benzylic amine oxidation and should be considered for future use in chemical synthesis as a green alternative.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures and characterization, as well as results of light mapping experiments are given in the supplementary information. The following files are available free of charge.

Supporting information (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

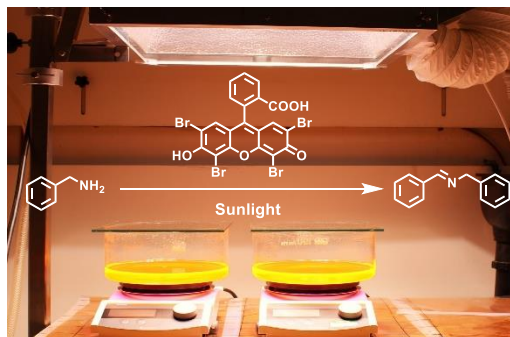
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The first in-depth study of eosin Y for photocatalytic oxidative coupling of benzylic amines using a solar light simulator.